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SYNTHESIS, LINEAR AND NONLINEAR OPTICAL PROPERTIES OF AG/PVP NANOCOMPOSITE

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ABSTRACT

In this study, silver nanoparticles were synthesized using sodium borohydride ($NaBH_4$) as a reducing agent at different concentrations (1 wt %, 2 wt %, 5 wt %) of poly N-vinylpyrrolidone (PVP) as a stabilizing agent by chemical reduction method.The reaction was carried at room temperature. Resulting nano-sized colloids have been characterized by FT-IR spectroscopy, UV-Visible spectroscopy, X-ray diffraction, and Transmission Electron Microscopy (TEM). Very strong surface Plasmon resonance peak at 410 nm in the UV-Visible is a direct evidence of formation of nano-sized silver colloids. XRD Diffraction pattern reveals the formation of cubic structured crystals.Transmission Electron Microscopy (TEM) confirms average diameter of silver nanoparticles as 9 nm. The non-linear refractive index (n_2) were calculated by Z-Scan technique using CW He-Ne laser (λ=632 nm)and are obtained as high as 3.353 x 10^{-4} cm^2/W,8.697 x 10^{-4} cm^2/W, and 9.469 x 10^{-4} cm^2/W for 1 wt%,2 wt% and 5wt% of PVP respectively.

KEYWORDS: Silver Nanocomposite, Nonlinear Refractive Index, UV-Visible, FTIR, XRD, TEM, Z-Scan Technique

INTRODUCTION

Noble metal nanoparticles received great attention and investigated widely due to their unique electronic, optical properties and potential applications in catalysis, biological and chemical sensing, nonlinear optics, surface-enhanced Raman Spectroscopy and electronics.Silver nanoparticles show surface plasmon resonance absorption in the ultraviolet and visible region. Plasmon resonance occurs from coherent existence of free electron in conduction band due to quantum confinement effect [1-5].Particle size, surrounding chemical environment and dielectric constant affect the Band shift.

Largenumbers of methods have been reported to synthesize silver nanoparticles in the literature, mainly reduction of silver ions by radiation gamma rays, ultra violet and visible light, chemical, electrochemical, laser ablation[7].The most popular method of synthesis of silver nanoparticles is chemical reduction method where silver salts are reduced by Sodium borohydride or sodium citrate. In this method the most challenging task is to control the size and shape of the metal nanoparticles. Other factors which influence the particle size are temperature of the solution, concentration of metal salt, reducing agent and reaction time. [7].Since the past decade, special efforts have been made in controllingthe shape, size and corresponding physical and chemical properties of silver nanoparticles. Optical properties of silver nanoparticles mainly depend on the nature and concentration of surfactant.[11]

Formation of stable silver colloidal dispersed in polymer matrix, can result in novel optical properties; have been of great research interest due to their potential applications in non-linear optics. The aim of this work is to develop highly

stable nanoparticles and to study their non-linear optical properties under CW He-Ne laser irradiation. Since Z-scan technique is extensively used to find nonlinear refractive index (n_2) due to its simplicity and accuracy, we have used it to calculate n_2.The synthesised particles were characterised bymeans of UV-Visible spectroscopy, FTIR, XRD, and TEM. [1-2]

EXPERIMENTAL

Chemicals

Silver nitrate ($AgNo_3$99% purity), Sodium borohydride ($NaBH_4$,98% purity),Poly-Vinyl pyrrolidone (PVP, 10000 mol. wt)were purchased from Aldrich and used without any further purification.$NaBH_4$ is used as reducing agent and PVP is used as stabilizing agent. De-ionised water was used to prepare stock solution of 2mM $NaBH_4$, 1mM $AgNO_3$, and 1wt%, 2wt%,5wt% PVP.

Synthesis of Silver Nanocolloids

In 200 ml volumetric flask, 30 ml de-ionised water and 10 ml $NaBH_4$ (2mM) which had already chilled into ice-bath for 20 minutes and further stirred for 20 minutes, is taken.Silver nanoparticles were obtained by drop wise addition of silver precursor (5 ml, 1mM) into mixture of aqueous solution of sodium Borohydride and PVP (1wt% ,2 wt%,5wt% PVP).Solution turned yellow in colour in 2 mins, then turned light green after 2 hrs,(stable colour) indicating formation of silver nanoparticles. Obtained colloids were stable for long time at least for 5 months [9]. Synthesis of Greenish-yellow colour silver nanoparticles is already reported.By spin coating method, thin films of 1wt%, 2 wt%,5wt% of PVP have been prepared at room temperature. Silver nanoparticles were prepared by the process of chemical reduction methodaccording to the reaction;

$$2AgNO_3 + 2NaBH_4 + 6H_2O \rightarrow 2Ag + 2NaNO_3 + 2H_3BO_3 + 7H_2O$$

UV-Vis absorption spectra were recorded on spectrometer (Model-Black-C-SR, Stellarnet Inc. USA) spectral range 190–1083 nm. X-Ray diffraction pattern were recorded with RigakuMiniplex-II X-Ray Diffractometer with Cu Kα=1.054 A.U. radiation for 2θ values of over 20^0- 70^0. FTIR spectra were obtained with machine 3000 hyperion microscope with vertex 80 FT-IR system (Bruker, Germany).TEM images were obtained using CM200 model (PHILIPS).

RESULTS AND DISCUSSIONS

UV-Visible Spectra

Due to surface Plasmon resonance vibration, silver nanoparticles absorb radiation in the range 380 nm – 450 nm which is the main reason for the appearance of green colour of silver nanoparticles [9]. Figure 1 shows UV-Vis absorption spectra of obtained silver nanoparticles stabilized in 1wt%, 2wt% and 5wt% of PVP. Spectra of silver colloids contains strong Plasmon band at 413nm, 410 nm and 406 nm for 1wt%, 2wt%and 5wt% of PVP, which confirms that silver ions were reduced to Ag^0 in aqueous medium.The degree of colloid aggregation decides Plasmon peak and its full width half maxima (FWHM)[10].We found that particle size reduced due to increasing amount of PVP.

From UV-Visible spectra we can conclude that, maximum absorption wavelength ($\lambda_{max.}$) shift towards smaller wavelength, showing blue shift as amount of PVP increases. It has been observed that position of maximum absorption wavelength i.e. $\lambda_{max.}$dependson particle size and concentration of stabilizing agent.

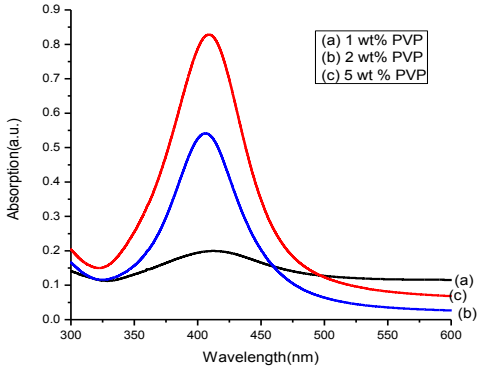

Figure 1: UV-Visible Absorption Spectra of Silver Nanoparticles Stabilized in (A) 1wt% PVP, (B) 2wt% PVP, (C) 5wt% of PVP

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) is carried out with prepared samples since it is a useful technique to study structure and structural transformation. An FTIR spectrum taken over the range 400 cm^{-1} - 4000 cm^{-1} of silver nano-colloids with PVP is as shown in Figure 2.

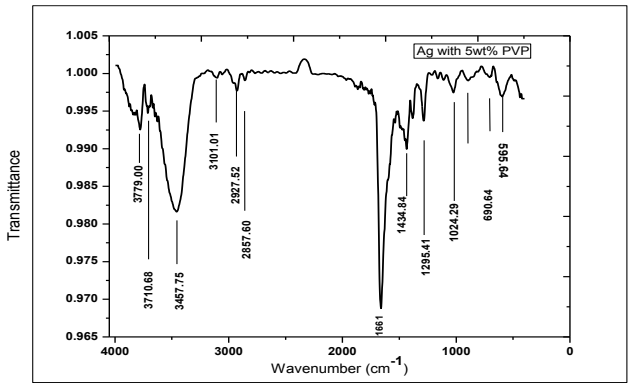

Figure 2: FTIR Spectra of Silver Nano Colloids with 5wt% PVP

As per literature, amide carbonyl stretchabsorption is in between 1615 cm^{-1} to 1695 cm^{-1}. All three samples (1wt% PVP, 2wt% PVP, 5wt% PVP) show common feature of strong absorption band at 1661 cm^{-1} which is attributed to amide carbonyl (C= O)from PVP. Absorption peak at 1434 cm^{-1} is due to vibration of tertiary nitrogen. Along with this, other absorption bands that appear at 2857 cm^{-1} and 2927 cm^{-1}, are attributed to symmetric and asymmetric stretching vibration of C-H band. Hydroxyl group absorb at 3580cm^{-1} – 3480 cm^{-1}. In the our sample O-H stretchingoccurred from 3457 $cm^{-1}$to 3779 cm^{-1}due to thepresence of water. Various C-H plane deformation bands exist in the region 1290cm^{-1}-1000cm^{-1}.These bands are not significant for interpretation purpose. In the samplefor 5wt%PVP, absorption peak due to C-H deformation is observed at 1024 cm^{-1} and 1285 cm^{-1}.The absorption frequencies ranging from 430 cm^{-1} to 760 $cm^{-1}$are assigned to C-C plane deformation vibration.Peak at 895$cm^{-1}$is due to C-C bond in PVP-silver matrix which is largely deviated due to presence of PVP nano silver matrix bonding.PVP being highly hydrophobic in nature, have high affinity towards Ag^{+} ions and hence form a covalent bond between pyridyl group and silver ion.[21] Coordination between silver nanoparticle and stabiliser i.e. PVP is suggested by presence of absorption band at 1024 cm^{-1}. This peak indicates that pyrrolidyl nitrogen electron is taking part in the formation of silver nanoparticles by donating electron from N to Agor coordination between these two atoms.[12-13].

Structural and Morphological Studies

Structural and morphological study has been done using X-Rd spectra of silver/PVP nanocomposite. Figure 2 shows X-Ray Spectra of thin film made up of silvernano particles stabilised in 1wt% PVP taken for 2θ ranging from 20^0 to 60^0.

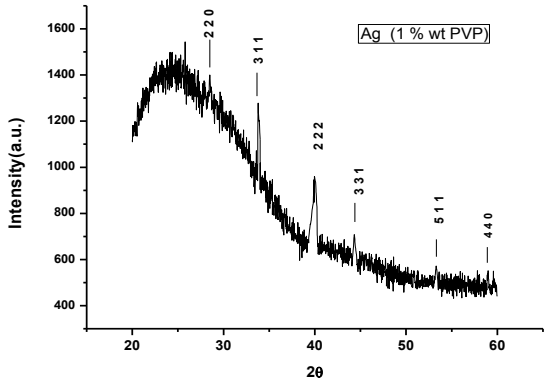

Figure 3: X-Ray Diffraction Pattern of Silver Nanoparticles Stabilised in 1wt% PVP

The main X-ray diffraction peaks were observed at 2θ = 28.503^0, 33.80^0,39.96^0, 44.31^0, 53.32^0, 58.99^0which corresponds to lattice planes (2 2 0), (3 1 1), (2 2 2), (3 3 1), (5 1 1),(4 4 0).Broad nature of curve is due to PVP existence. Moreover XRD pattern reveals the cubic crystal structure of silver nanoparticles which matches with JCPDS 01-1164.Cubic structured silver nanoparticles in PVP is already reported in(674). The lattice parameter is found to be a = b= c = 4.079 and unit cell volume V=67.87. The diffraction peaks of as prepared silver nano composite is broaden as compared to bulk silver,indicating formationof small crystalline size of silver particles. Absence of Ag_2O peaks in X-Rd pattern indicatesnon –oxidation of silver during the reaction. From full width at half maximum of diffraction peaks, average of silver nanoparticles is calculated by using Debye- Scherrer Equation.( ) The average size is found around 9 nm.The crystalline nature of silver nanoparticles is further confirmed by transmission electron microscopy (TEM). Figure 4 shows TEM images along with diffraction pattern. From TEM image, average size of silver nanoparticles is found as 8.5nm.

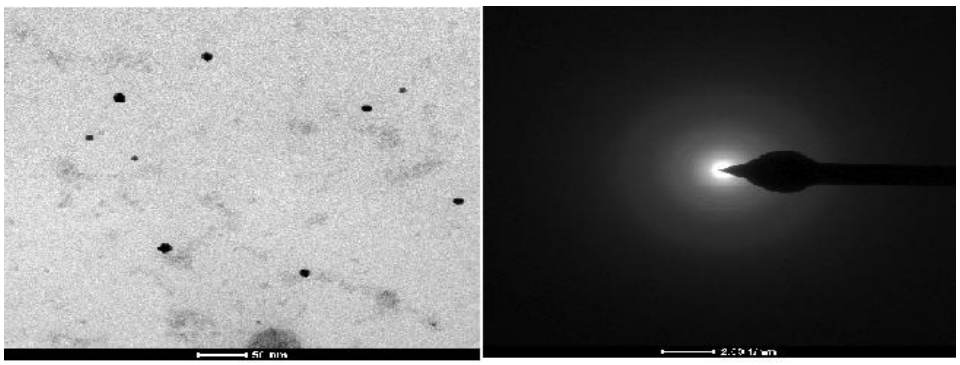

Figure 4: (a) TEM Image of Silver Nanoparticle (b) SAED Pattern from Silver Nanoparticles

Nonlinear Optical Properties Measurement

Nonlinear optical properties of as prepared nano-sized silver/PVP composite are investigated by using famous Z-scan technique [15].The schematic diag. of open aperture Z-scan set up is as shown in Figure

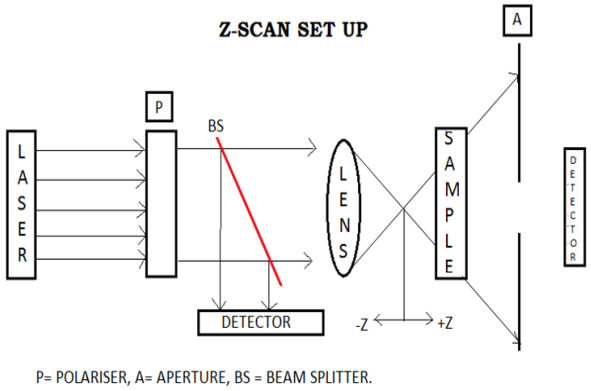

Figure 5

The non-linear refractive index$\eta_2$was calculated by Z-Scan technique using CW He-Ne laser of wavelength 632 nm.To find beam waist, sample were taken in quartz cuvette of 1mm path length and moved across the focal point of lens. The beam waist is found to be beam waist, ω_0 =22 μm and Rayleigh range, z_0=2.4 mm. The required condition$\frac{\pi \omega_0^2}{\lambda} > \mathbf{L}$ is satisfied by thin film, where ω_0 is beam waist at the focal point, L is thickness of sample and λ is the wavelength of laser light used.

Nonlinear absorption coefficient β can be measured by fittingnormalised transmittance data into the formula given by Sheik-Bahae*et al*,1989 and Sheik-Bahae*et al*, 1990;[15].

$$T(Z, S=1) = \sum_{m=0}^{\infty} \sum_{m=0}^{\infty} \frac{[-q_o(Z)]^m}{(m+1)^{3/2}} |q_o(z)|<1, \quad (1)$$

Where, $q_o(z) = I_o \beta L_{eff} / [1+(\frac{Z}{Z_o})^2]$, $Z_o = \frac{k\omega_o^2}{2}$, is the diffraction length of the beam = 2.4 mm in this experiment, $k = 2\pi/\lambda$, is the wave vector, ω_o = The beam waist radius at the focal point, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, is the effective thickness of the sample, β is the non-linear absorption coefficient, I_0 is the intensity of laser atfocus z=0,α is the linear absorption coefficient, L is thickness of the sample. In this experiment L_{eff}= 100mm.

The nonlinear refractive index η_2 can be measured from the normalised transmittance data of the closed aperture measurement which can be written as follows (Sheik- Bahae et.al., 1990):

$$T(Z,\Delta\phi) = 1 - \frac{4\Delta\phi_0 x}{(x^2+1)(x^2+9)} \quad (2)$$

The nonlinear refractive index η_2 is given by,

$$\eta_2 = \frac{\Delta T_{P-V}}{0.464(1-S)^{0.25} k L_{eff} I_o} \quad (3)$$

Where λ is wavelength of laser, ΔT_{P-V}difference between normalised peak and valley transmittance, which can be calculated as 0.4354, 0.3967,and 0.4319, for sample 1wt% PVP, 2wt% PVP and 5wt% of PVP from best theoretical fit and is shown in Figure 5 (a) ,5(b) and 5(c).$S$is the aperture linear transmittance.

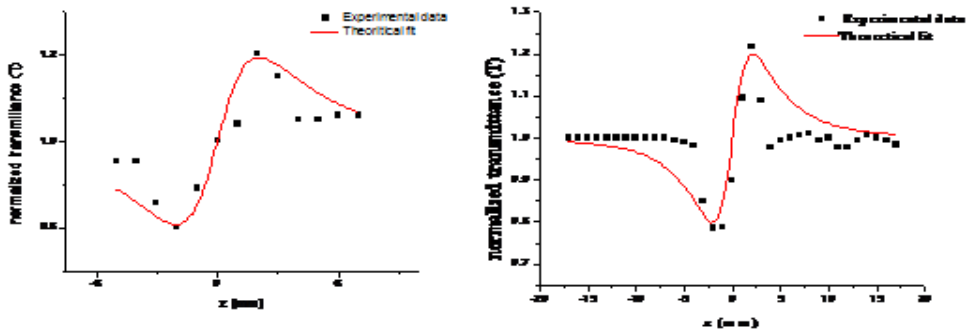

Figure (a) **Figure (b)**

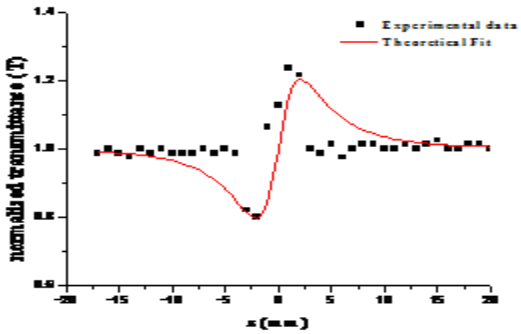

Figure (c)

Figure 6: Normalised Z-Scan Curve (Close Aperture) of Silver Nano Particles at (a) 1wt% PVP (b) 2wt% PVP (c) 5wt% PVP

The third order nonlinear refractive index is to be calculated as 3.353 x 10^{-4} cm^2/W,8.697 x 10^{-4} cm^2/W,and 9.469 x 10^{-4} cm^2/W respectively.Nonlinear refraction is major because of silver/PVP colloids since non-linear refraction of solvent is small and hence negligible.[16-20]. Particle size of silver nanoparticledecreases with increase in wt% of PVP and we have found that nonlinear refractive index increases for 1 wt%, 2wt%, 5wt% of PVP.

Table 1: Calculated Values of η_2 at Different Concentration of PVP

Sample	Amount of PVP	Conc. of $NaBH_4$	I_0(KW/Cm^2)	$\Delta\phi_0$	ΔT_{p-v}	η_2 (cm^2/W)
A1	1wt%	2mM	1.315	- 0.9999	0.4354	3.353 x 10^{-4}
A2	2wt%	2mM	1.315	-0.9500	0.3967	8.697 x 10^{-4}
A3	5wt%	2mM	1.315	-0.9900	0.4319	9.469 x 10^{-4}

CONCLUSIONS

Silver nanoparticles reduced in $NaBH_4$, stabilised in different concentrations of PVP is synthesisedsuccessfully by chemical reduction method. Surface plasma resonance band of silver nanoparticle is found at 413 nm, 410nm, and 406 nm for 1wt%, 2wt% and 5wt% of PVP and shows blue shift.FT-IR spectra confirms the coordination between silver nanoparticle and stabiliser i.e. PVP, suggested by presence of absorption band at 1024 cm^{-1}.XRD peaks reveal the formation of cubic centred crystals and average size of nanoparticles is found to be8.5 nm by Debye-Schurrer equation, which is further confirmed by TEM Images. From TEM Images, average size is calculated at around 9 nm. Nonlinear refractive index of silver nanoparticles is found to be as high as3.353 x 10^{-4} (cm^2/W), 8.697 x 10^{-4} cm^2/W, and 9.469 x 10^{-4} cm^2/W for 1wt%, 2wt% and 5wt% of PVP and it is positive. We have found that nonlinear refractive index increases with increase in PVP wt%. High positive nonlinear refractive index is due to thermo-optic effect and it shows self- focussing phenomenon.

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